

REMARKS

The Applicant appreciates the Examiner's quick and courteous Action.

Claims 1-33 are pending in the application. Claims 1-33 stand rejected. Claims 1, 7, 9, 12, 14, 17, 22, 25, 27, 29 and 32 are amended herein. No new matter is added.

The Applicant respectfully requests reconsideration in view of the following remarks.

Rejection Under 35 U.S.C. §103 over Awbrey, et al. in view of Ohsol

The Examiner has rejected claims 1-33 under 35 U.S.C. §103(a) as allegedly being unpatentable over U.S. Pat. No. 5,080,779 to Awbrey, et al. in view of U.S. Pat. No. 4,938,876 to Ohsol in view of U.S. Pat. No. 2,175,095 to Stoesser.

[Applicants believe that the reference to Stoesser is an inadvertent error on the Examiner's part because the rejection does not otherwise mention Stoesser except to say that it has been withdrawn as a reference since the Examiner agreed that it was non-analogous art.]

The Examiner contends that Awbrey, et al. discloses a method, a composition and emulsion for removing metals from a hydrocarbon phase to a water phase involving adding between about 18 ppm of a chelating agent to water and adding the water mixture to crude oil to create an emulsion and separating the emulsion into a hydrocarbon phase and an aqueous phase containing at least a portion of the metals. The Examiner finds that Awbrey, et al. discloses where the desalters commonly contain electrodes to impart an electric field in order to promote coalescence.

The Examiner admits that Awbrey, et al. does not disclose where the chelating agent is glycolic acid and does not disclose where a mineral acid is added to lower the pH of the wash water to 6 or below.

However, the Examiner finds that Ohsol discloses where the chelating agent is glycolic acid, and that glycolic acid is used to remove metal contaminants from oil into a water phase.

Therefore, the Examiner alleges that it would have been obvious to one having ordinary skill in the art at the time of the invention to modify the invention of

Awbrey, et al. to include where the chelating agent is glycolic acid in order to remove metal contaminants from oil into a water phase.

In response to the Applicants' arguments, the Examiner notes that the Applicants first argue that Ohsol is concerned with a different process than that of Applicants and thus there would be no motivation to combine Ohsol, which discloses separating oil and water waste oil emulsions, with the reference of Awbrey, et al., which discloses refinery desalting of crude oil using electrostatic coalescence. However, in response to Applicants' argument that Ohsol is nonanalogous art, the Examiner asserts that it has been held that a prior art reference must either be in the field of applicant's endeavor or, if not, then be reasonably pertinent to the particular problem with which the applicant is concerned in order to be relied upon as a basis for rejection of the claimed invention (citing *In re Oeticker*). The Examiner contends that in this case Ohsol, which discloses that glycolic acid is used to remove metal contaminants from oil into a water phase is reasonably pertinent to the particular problem with which Applicants were concerned, transferring metals from a hydrocarbon phase to an aqueous water phase.

Second, the Examiner finds that Applicants argue that there is no suggestion or motivation to combine Ohsol with Awbrey, et al. In response, the Examiner recognizes that obviousness can only be established by combining or modifying the teachings of the prior art to produce the claimed invention where there is some teaching, suggestion, or motivation to do so found either in the references themselves or in the knowledge generally available to one of ordinary skill in the art (citing *In re Fine*). In this case, the Examiner contends that Ohsol discloses that glycolic acid is used to remove metal contaminants from oil into a water phase, and apparently this is sufficient suggestion or motivation to combine the references.

Third, the Examiner notes that Applicants argue that Ohsol does not recognize the important nature of pH taught in Applicants' methods and compositions. However, the Examiner contends that the fact that the applicant has recognized another advantage which would flow naturally from following the

suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious (citing *Ex parte Obiaya*). Apparently the Examiner considers “lowering the pH of the wash water” to be an advantage, rather than an element or feature recited in the claims, and that such advantage “flows naturally” from the cited art.

The Applicants would respectfully traverse.

To support an obviousness rejection, the Examiner has the initial burden of establishing a *prima facie* case of obviousness of the pending claims over the cited prior art, *In re Oeticker*, 977 F.2d 1443, 1445; 24 U.S.P.Q.2d 1443 (Fed. Cir. 1992). Applicants respectfully submit that the Examiner has not established a *prima facie* case of obviousness of the claims herein, as amended, as will be established.

The Examiner’s attention is respectfully directed to independent method claims 1, 7, 22, and 25 which have been amended to further define that the method additionally comprises “lowering the pH of the wash water to 6 or below, before, during and/or after adding the composition”. Support for this language is found in dependent claims 4 and 8 and in paragraph [0028] on pages 10-11 of the application as originally filed and elsewhere and thus does not constitute an improper insertion of new matter. There are no limitations about when the pH of the wash water is lowered and thus the lowering may properly be before, during and/or after adding the composition.

The Examiner’s attention is further respectfully directed to independent composition claims 9, 12, and 27 where the pH of the composition is now recited 6 or below. The further recitation of the pH range does not constitute an improper insertion of new matter to these claims because this language was present in the application as originally filed; again please see paragraph [0028]. Similarly, independent composition claims to treated hydrocarbon emulsions 14, 29 and 32 further recite a wash water having a pH of 6 or below.

The Examiner’s attention is respectfully directed to Awbrey, et al. where their data indicates that pH is not a factor in their process. The Examiner’s

attention is respectfully directed to the paragraph bridging columns 6 and 7 therein where it is noted:

In several instances, as shown in the Table, pH control agents, specifically, NaOH or H₂SO₄, were added to the wash water until a specified pH was attained. This was done in an attempt to establish if the pH of the wash water had any bearing on iron removal efficacy.

Apparently Awbrey, et al. concluded that the pH of the wash water did not have any bearing on iron removal efficacy since it was not further mentioned. Further, Awbrey, et al.'s Table I data discloses a pH of 3.5 (column 7, lines 38-40), but it is *not* with Awbrey, et al.'s chelating agent present. This data point only includes sulfuric acid and an emulsion breaker. Indeed, the data in Awbrey, et al.'s Table I shows iron reduction of the *high pH* solution to be *better* than that at a *low pH* solution, which is what is now recited in the claims amended herein. The Fe ppm reduction for the reference at 3.5 pH (lines 38-40) is only 2.6 (calculated as initial iron in crude 6.60 ppm – 4.0 Crude Fe out), as compared with 3.1 reduction for pH of 10.5 (reference at lines 36-37 of column 7) and 3.2 reduction again for pH of 10.5 (reference at lines 49-50 of column 7). It thus appears that Awbrey, et al. *teach away from* the pH range now recited in the claims as amended herein.

A reference which leads one of ordinary skill in the art away from the claimed invention cannot render it unpatentably obvious. *Dow Chemical Co. v. American Cyanamid Co.* 816 F.2d 617, 2 U.S.P.Q.2d 1350 (Fed. Cir. 1987); *In re Grasselli, et al.*, 713 F.2d 731, 218 U.S.P.Q. 269 (Fed. Cir. 1983); *In re Dow Chemical Co.* 837 F.2d 469, 5 U.S.P.Q.2d 1529 (Fed. Cir. 1988).

Ohsol is no help in teaching that pH is important since the only mention of pH therein is at column 7, lines 59-61 which only generally and simply speaks of using pH adjustment and precipitation to precipitate chelated metals present in the aqueous phase. There is no teaching in which direction the pH adjustment should be. This is not particularly surprising since the Ohsol reference does not involve refinery desalting processes using electrostatic coalescence, or the treatment of crude oil, but rather methods for separating oil and water in *waste oil* emulsions. The Examiner's attention is respectfully directed to column 1, lines 1-7 therein:

The invention relates to the purification and separation of oil, water and solids from *waste oil*. This *waste oil* can be found in many forms and is particularly found in large quantities as storage tank bottoms and in lagoons where waste oil has historically been transferred for storage. (Emphasis added.)

The Ohsol emulsions contain 5 to 80% water (column 4, lines 59-62) filled with solids such as inorganic salts, dirt, etc. (column 1, lines 43-47, and column 4, lines 13-23). Ohsol concerns a process to clean up slop oil or waste oil by the use of temperature drops (please see Abstract and the FIG.), pressure drops (please note flashing in claim 1 therein), centrifuges (continuous centrifuge 42; please see column 7, lines 5-30; column 10, lines 43-46; claim 39; all Examples and the FIG.) and hydrocyclones (please see column 3, lines 59-63; hydrocyclones 28 and 29; please see column 6, line 42 to column 7, line 4; and the FIG.).

The pH is important to the partitioning of counter-ions, such as naphthenic acid, out of the water and into a protonated form that releases the metal species. The pH is also important to liberate the metal from the organometallic species present in the system. The claimed compositions (chelating agents) have to be able to displace the original chelating agent on the metal (usually present) in the crude oil, and pH is an important driver of this process. Again, please see paragraph [0028] on pages 10-11 of the application as filed.

The Applicants would further respectfully direct the Examiner's attention to U.S. Pat. No. 5,282,959 to Roling, et al. enclosed herewith. This document discloses a method for extracting iron species from a hydrocarbon by adding to it a composition including an aminocarboxylic acid, methoxypropylamine and a solvent (Abstract). Roling, et al. indicates that optimal desalter pH values are between 6-10 (column 3, lines 25-28) in contrast to the lower range now recited in the amended claims. Thus, the Applicants are once again claiming what those skilled the art suggest should not be done. *Kloster Speedsteel AB v. Crucible Inc.*, 793 F.2d 1565, 230 U.S.P.Q. 81 (Fed. Cir. 1986), *on rehearing*, 231 U.S.P.Q. 160 (Fed. Cir. 1986) instructs that the inventor achieving the claimed invention by

doing what those in the art suggested should not be done is a fact strongly probative of nonobviousness.

The Applicants herein also have respectfully included the following documents herein that describe the present inventive technology, termed EXCALIBURSM metals removal technology, all of which have been published since the instant application was filed:

- J. Weers, et al., "A New Metals Removal Process for Doba Crude Oil," *ERTC 9th Annual Meeting*, Prague, Czech Republic, November 15, 2004.
- J. Weers, et al., "Calcium Removal from High TAN Crudes," *Petroleum Technology Quarterly*, Q3 2005, available from www.eptq.com.
- Baker Petrolite, "Remove Metals, Improve Margins", EXCALIBUR brochure, 2005.

The Applicants would especially note from the ERTC paper the following portions:

- Page 4, Table 6 and the text just prior thereto teaching:

The results (Table 6) suggested the lower the initial pH of the wash water the better the metals removal. The effluent pH values trended with the initial pH results in that lower effluent values were associated with better metal removal efficiency. (Emphasis added.)

- Page 9, first paragraph: "Variables which favored *increased calcium removal* when they *decreased* included crude charge rate, alkalinity (amine) content of the wash water and *desalter effluent pH*. (Emphasis added.)"
- Page 11, the paragraph below Figure 4; please also see the Conclusions on page 14:

Controlling effluent pH is key to successful metals removal. During the trial, the high alkalinity of the wash water made decreasing the effluent pH difficult but when the pH was between 5.0 and 6.0, the calcium removal

efficiency ranged from 66 to 100% removed with the best results being at the lowest pH. (Emphasis added.)

Roling, et al. also indicates that adding amines (e.g. EDTA and NTA) improves metal removal. While Roling, et al. recommends *adding* amines (as does Awbrey, et al., which also teaches using EDTA and NTA as chelants) the Applicants herein have instead discovered that the water-soluble hydroxyacids recited herein *remove* them as claimed. Indeed, the Applicants respectfully submit that there is no disclosure, teaching or hint of record about a method that removes amines from a hydrocarbon phase to a water phase, much less a method that removes amines and/or metals from a hydrocarbon phase to a water phase.

The Applicants would additionally respectfully direct the Examiner's attention to the claims herein which require that the effective composition is added to a wash water, as contrasted with adding the composition to the crude oil. Contrary to the Examiner's contention, the latter is the procedure exclusively used by Awbrey, et al., the primary and most pertinent reference of record. Awbrey, et al. in the only independent claim, claim 1 requires: "In a two-stage desalting system having an upstream and downstream desalter and wherein a crude oil/water emulsion is formed and resolved in said upstream desalter with crude separated from said upstream desalter being fed to said downstream desalter, *a method for decreasing iron content of said crude comprising, mixing a water soluble chelant with said crude ...*" (emphasis added).

Even more instructive is how Awbrey, et al. distances and distinguishes their method from the prior art. The Examiner's attention is respectfully directed to column 3, lines 15-31:

PRIOR ART

Chelant addition to wash water for mixture with crude prior to entry of the emulsion into a desalter is known. Chelant chemistries, however, are not surface active and, as a result, the efficiency of contacting the chelant molecules with iron in the crude-water admixture is low, resulting in exorbitant and uneconomical chelant addition requirements.

In U.S. Pat. No. 4,853,109 (Reynolds), dibasic carboxylic acids, such as oxalic, malonic, succinic, maleic, and adipic acid are used as

chelants to remove metals, primarily calcium and iron, from hydrocarbonaceous feedstocks. *Here, in accordance with conventional wisdom, the feedstock is mixed with an aqueous solution of the dibasic carboxylic acid as opposed to direct feed of the chelant into the crude, followed by addition of water.* (Emphasis added.)

Awbrey, et al. goes against what they call "conventional wisdom" and insists the chelant is to be added to the crude, not the wash water. Please see column 2, lines 42-46:

The chelant should be fed directly to the crude. Sufficient time is then given for the crude/chelant combination to adequately mix. *Then, wash water is admitted to the mixed crude/chelant combination with the chelated iron moieties partitioning to the water phase.* (All emphasis added.)

As noted, in contrast to the method defined in Awbrey, et al., Applicants add the effective composition *to the wash water*, which is then in turn added to the crude. Evidence that this method is superior to that of Awbrey, et al. is provided in the attached 37 CFR §1.132 Declaration of co-inventor Tran Nguyen. As detailed therein, two experiments were conducted identically, except that in Sample # 170117-001 the glycolic acid (the water-soluble hydroxy acid) was initially added into the crude oil, whereas in Sample # 170117-002 the glycolic acid was initially added into the wash water. As shown in the attached Core Laboratories report of January 12, 2007, the iron content from Sample # 170117-001 where the glycolic acid was added into the crude oil was 3.58 mg/kg, as contrasted with the iron from Sample # 170117-002 where the glycolic acid was added into the wash water which was only 1.72 mg/kg; *less than half that* of Sample # 170117-001. It must thus be concluded that where the glycol acid was added in the method made a significant difference in how much iron was removed, and that adding the glycolic acid to the wash water, as recited in the claims as amended herein is an important and surprising improvement over adding it to the crude, according to the method disclosed and required by Awbrey, et al.

"One way for a patent applicant to rebut a *prima facie* case of obviousness is to make a showing of 'unexpected results,' *i.e.*, to show that the claimed

invention exhibits some superior property or advantage that a person of ordinary skill in the relevant art would have found surprising or unexpected.” *In re Soni*, 54 F.3d 746, 750, 34 U.S.P.Q.2d 1684, 1687 (Fed. Cir. 1995) cited in *In re Gluag*, 283 F.3d 1335, 1341; 62 U.S.P.Q.2d 1151 (Fed Cir. 2002). The Applicants respectfully submit that the data presented in the attached Declaration is evidence of unexpected results thus rebutting the Examiner’s case of obviousness.

Further with respect to Ohsol, the Applicants respectfully submit that the crude oils treated and separation methods and compositions recited in the claims as amended herein are different from the waste or slop oils addressed in Ohsol and the separation techniques disclosed therein. Particularly with respect to the method claims the composition (e.g. glycolic acid) is added to wash water (not an emulsion as in Ohsol), this water is then added to *crude oil* (not slop oil or waste oil) and an emulsion is created and the emulsion is resolved using *electrostatic coalescence* to remove the metals and/or amines. The methods claimed herein do not involve slop oil or waste oil emulsions or a method for separating such emulsions using centrifuges and hydrocyclones as required by Ohsol. Further, the emulsions herein relate to crude oil, not to slop oil or waste oil.

Applicants again respectfully submit that because Ohsol and Awbrey, et al. are different processes, there is no motivation for one having ordinary skill in the art to consider combining the disclosures therein. Awbrey, et al. is entirely focused upon extracting *iron* from liquid hydrocarbons; please see the title, Abstract, Examples, claims and elsewhere. In contrast, Ohsol does not teach, disclose, suggest or exemplify extracting iron. While Ohsol mentions that the solids suspended in the waste oil may contain ferric compounds at column 4, lines 13-23 (ferric phosphate, ferric hydroxide), it is never taught, suggested or shown that iron species may be removed by the Ohsol process. Vanadium is shown to be removed or sequestered by the Ohsol process in Example 3, but not iron. (Ferric chloride is taught as added to the *water* in a conventional water treatment procedure; please see column 7, lines 29-35 and column 12, lines 52-55.) Applicants thus respectfully submit that one having *ordinary* skill in the art attempting to improve the Awbrey, et al. process for removing iron from crude oil

would not think to use any teaching of Ohsol since Ohsol teaches and shows nothing about removing iron from crude – it only teaches that ferric phosphate and ferric hydroxide may be suspended solids in the waste or heavy residual oils, *not* how to remove them from the waste oils. Ohsol is further not reasonably pertinent to the *Applicants'* technical problem either since it has nothing to do with improving a refinery desalting process. Awbrey, et al. is only concerned with removing iron from crude oil and Ohsol does *not* disclose anything about sequestering iron from waste oils or slop oils. There is thus no motivation for modifying the Awbrey, et al. to include any procedure or components of Ohsol

“The mere fact that the prior art could be so modified would not have made the modification obvious unless the prior art suggested the desirability of the modification.” *In re Gordon*, 733 F.2d 900, 902, 221 U.S.P.Q. 1125, 1127 (Fed. Cir. 1984) cited in *In re Mills*, 916 F.2d 680, 16 U.S.P.Q.2d 1430 (Fed. Cir. 1990), in turn cited by MPEP §2143.01. A reason, suggestion or motivation to combine the teachings of the references must be present to support a *prima facie* rejection of obviousness. *Alza Corp. v. Mylan Laboratories, Inc.* 391 F.3d 1365, 1372-1373 (Fed. Cir. 2004).

“Our reviewing courts have often advised the Patent and Trademark Office that it can satisfy the burden of establishing a *prima facie* case of obviousness *only* by showing some objective teaching in either the prior art, or knowledge generally available to one of ordinary skill in the art, that ‘would lead’ that individual ‘to combine the relevant teachings in the references.’ Accordingly, an examiner *cannot* establish obviousness by locating references which describe aspects of a patent applicant’s invention without *also* providing *evidence of the motivating force which would impel one skilled in the art to do what the patent applicant has done.*” [Citations omitted; emphasis added.] *Ex parte Levengood*, 28 U.S.P.Q.2d 1300, 1302 (B.P.A.I. 1993).

Applicants respectfully submit that herein there is no reason, suggestion or motivation to combine the teachings of the references, and in particular no evidence of the motivating force which would *impel* one skilled in the art to do what the Applicants have done. Further, Applicants respectfully submit that one of *ordi-*

nary skill in the art seeking to improve the Awbrey, et al. iron removal process would not look to Ohsol which does not disclose anything useful about *desalting systems for crude oil or removing iron from anything*, but rather only addresses sequestering a few metal species (Na, Ca, V, Ni, Cr mentioned in column 1, lines 26-27 – where only V is sequestered in Example 3) from waste oil or slop oil emulsions and then only by using temperature drops, pressure drops, centrifuges and hydrocyclones – not desalters.

For all of these reasons, Applicants respectfully submit that the Examiner has not made a *prima facie* case of obviousness for the claims as amended over the art cited. Reconsideration is respectfully requested.

Supplemental Information Disclosure Statement

It is respectfully submitted that the art listed on the enclosed PTO/SB/08A be considered in the examination of the subject application and made of record herein.

No representation is made or intended that a search has been made or that no better art than is listed is available. All of the art is in English, and thus no explanation of its relevance is required.

The Supplemental Information Disclosure Statement transmitted herewith is being filed *after* three months of the filing date of this national application or the date of entry of the national stage as set forth in §1.491 in an international application or after the mailing date of the first Office Action on the merits, whichever event occurred last but *before* the mailing date of either:

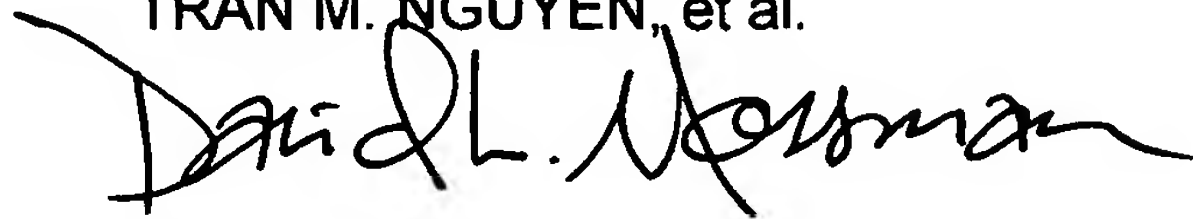
- (1) a final Action under §1.113 or
- (2) a Notice of Allowance under §1.311, whichever occurs first.

Accompanying this transmittal is the fee set forth in 37 CFR §1.17(p) for submission of an Information Disclosure Statement under §1.97(c) (\$180.00).

It is respectfully submitted that the arguments presented above overcome the rejection. Reconsideration and allowance of the claims are respectfully requested. The Examiner is respectfully reminded of his duty to indicate allowable

subject matter. The Examiner is invited to call the Applicants' attorney at the number below for any reason, especially any reason that may help advance the prosecution.

Respectfully submitted,
TRAN M. NGUYEN, et al.

A handwritten signature in black ink, appearing to read "David L. Mossman". The signature is fluid and cursive, with a long horizontal stroke at the end.

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United States Patent [19]

Roling et al.

[11] Patent Number: 5,282,959

[45] Date of Patent: Feb. 1, 1994

[54] METHOD FOR THE EXTRACTION OF IRON FROM LIQUID HYDROCARBONS

[75] Inventors: Paul V. Roling, Spring; Cato R. McDaniel, The Woodlands, both of Tex.

[73] Assignee: Betz Laboratories, Inc., Trevose, Pa.

[21] Appl. No.: 851,586

[22] Filed: Mar. 16, 1992

[51] Int. Cl.⁵ C10G 17/04

[52] U.S. Cl. 208/251 R; 208/252; 208/282; 208/289; 208/291

[58] Field of Search 208/251 R, 252, 282, 208/289, 291

[56] References Cited

U.S. PATENT DOCUMENTS

4,778,590 10/1988 Reynolds et al. 208/252
4,778,592 10/1988 Reynolds et al. 208/252
4,853,109 8/1989 Reynolds 208/252

Primary Examiner—Mark L. Bell

Assistant Examiner—Walter D. Griffin

Attorney, Agent, or Firm—Alexander D. Ricci; Gregory M. Hill

[57] ABSTRACT

A method of extracting iron species from a liquid hydrocarbon medium comprising adding to the medium a composition comprised of an aminocarboxylic acid, methoxypropylamine and a solvent selected from the group consisting of 2-ethylhexanol, cresylic acid, ethylene glycol and hexylene glycol.

2 Claims, No Drawings

METHOD FOR THE EXTRACTION OF IRON FROM LIQUID HYDROCARBONS

FIELD OF THE INVENTION

The present invention relates to the removal of undesirable iron contaminants from liquid hydrocarbons. It is especially helpful to remove iron species from crude oil prior to or during refinery processing.

BACKGROUND OF THE INVENTION

Liquid hydrocarbon mediums, such as crude oils, crude fractions, such as naphtha, gasoline, kerosene, jet fuel, fuel oil, gas oil and vacuum residuals, often contain metal contaminants that, upon processing of the medium, can catalyze undesirable decomposition of the medium or accumulate in the process residue. Accumulation of iron contaminants, like others, is undesirable in the product remaining after refinery, purification, or other processes and, accordingly, diminishes the value of such products.

Similar iron contamination problems are experienced in conjunction with other liquid hydrocarbons, including aromatic hydrocarbons (i.e., benzene, toluene, xylene), chlorinated hydrocarbons (such as ethylene dichloride), and olefinic and naphthenic process streams. All of the above petroleum feedstock and fractions and petrochemicals are referred to herein as "liquid hydrocarbon mediums."

Iron in such liquid hydrocarbon mediums may occur in a variety of forms. For example, it may be present as a naphthenate, porphyrin, or sulfide. In any case, it is troublesome. For example, residuals from iron-containing crudes are used, inter alia, to form graphite electrodes for industry. The value and useful life of these electrodes is diminished proportionately with the level of undesirable iron contamination.

Additionally, in many processes iron-containing catalysts are used which may carry over with the product during purification. Iron catalyst contaminated product leads to deleterious effects.

RELATED ART

It is well known that inorganic acids, at low pHs, will extract organic phase dissolved species into the water phase.

In Reynolds U.S. Pat. No. 4,853,109, it is taught that dibasic carboxylic acids, including oxalic acid, are added to a hydrocarbon feedstock in the form of an aqueous solution comprising the oxalic acid. In this disclosure, the oxalic acid is dissolved in water and then added to the crude. Separation of the w/o emulsion so formed is usually achieved in a desalter although countercurrent extraction techniques are also mentioned.

Other prior art patents that may be of interest include: U.S. Pat. No. 4,276,185 (Martin) disclosing methods of removing iron sulfide deposits from surfaces by using, inter alia, oxalic or citric acid; and U.S. Pat. No. 4,548,700 (Bearden et. al.) disclosing a slurry hydroconversion process in which a hydrocarbon charge is converted to a hydroconverted oil product. In Bearden et. al., a heavy oil portion of the products is separated and partially gassified to produce a carbon-free metal-containing ash that is extracted with oxalic acid. The resulting metal containing oxalic acid extract is recycled to the hydroconversion zone as catalyst precursor.

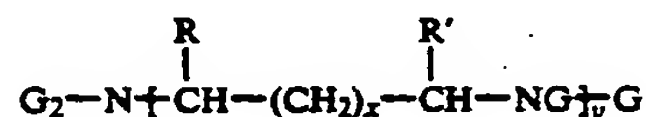
SUMMARY OF THE INVENTION

The present invention provides enhanced iron removal from liquid hydrocarbons by the use of an amino carboxylic acid and methoxypropylamine (MOPA) dissolved in a select group of hydroxyl containing solvents.

DETAILED DESCRIPTION OF THE INVENTION

Amino carboxylic acids are substantially insoluble in oil. We have discovered that by blending certain members of this group with MOPA into a specific solvent, iron contaminant removal from the hydrocarbon medium is enhanced.

The amino carboxylic acids useful according to the present invention may be defined as having the structure:



where $G=CH_2COOH$, $x=0$ or 1 , $y=0$ or 1 and R and R' may be the same or different and are H , alkyl or alkylene groups. Examples of such acids include ethylenediamine tetraacetic acid (EDTA, where $R=R'=H$, $x=0$, $y=1$), nitrilotriacetic acid (NTA, where $y=0$), (1,2-pyropylenedinitrilo)- N,N,N',N' -tetraacetic acid ($R=CH_3$, $R'=H$, $x=0$, $y=1$), (1,3-pyropylenedinitrilo)- N,N,N',N' -tetraacetic acid ($R=R'=H$, $x=1$, $y=1$), (2,3-butylenedinitrilo)- N,N,N',N' -tetraacetic acid ($R=R'=CH_3$, $x=0$, $y=1$) and 1,2-diaminocyclohexane- N,N,N',N' -tetraacetic acid (R and $R'=CH_2CH_2CH_2CH_2$, $x=0$, $y=1$). The preferred amino carboxylic acids are EDTA and NTA.

The formulation of the composition of the invention comprises about 2 to 20 weight percent of amino carboxylic acid based on the total composition. The amount of MOPA present in the inventive formulation will be about 3 to 30 weight percent based on the total composition.

The remainder of the composition comprises a hydroxyl containing solvent. Those solvents meeting the necessary requirement of being able to dissolve the MOPA:EDTA (or NTA) complex were found to be 2-ethylhexanol, cresylic acid, ethylene glycol and hexylene glycol.

Other solvents were tested for their ability to dissolve the MOPA/EDTA (or NTA) complex. Those include methyl t-butyl ether, isopropyl alcohol, acetonitrile, sulfolane, diglyme, triglyme, heavy aromatic naphtha and N-methylpyrrolidone. None of these other solvents exhibited the ability to dissolve, either partially or fully, the complex.

The ability of the amine (MOPA) and the amine carboxylic acid to become solubilized by the solvent is a critical element in the effective functioning of the present invention. Other amines were blended with EDTA (approximately 10% by weight) and attempts were made to dissolve the blend into one or more of the solvents disclosed above as being able to dissolve the MOPA/amino carboxylic acid blend. Table I shows the results.

TABLE I

Solvent	Solubility of other Amines	
	Amines having little or no solubility	
2-ethylhexanol	n-octylamine, ethylenediamine, tallowamine	
cresylic acid	aniline	
hexylene glycol	n-octylamine, ethylenediamine, tallowamine	
	aniline	

We have found that the introduction of the above formulation directly into the liquid hydrocarbon medium, in an amount of from 1-10 moles based upon each mole of iron present in the liquid hydrocarbon medium is most effective.

After the formulation is added to and mixed with the liquid hydrocarbon, water is added to the resulting mixture in an amount of about 1-15% water based on the weight of the liquid hydrocarbon. Preferably, water is added in an amount of about 5-10 wt. %. The w/o (water-in-oil) emulsion thus formed is resolved with iron laden aqueous phase being separated. Reduced iron content hydrocarbon phase may be then subjected to further processing prior to end-use or it may be directly used for its intended end purpose as a fuel, etc.

Preferably, the emulsion is resolved in a conventional desalter apparatus. In typical desalters, optional pH operating conditions are maintained at from about 6-10 in order to retard corrosion and enhance emulsion resolution. Conventional desalters also utilize heat treatment and electric fields to aid in emulsion resolution. The methods of the present invention provide improvement in iron removal at such operating pHs and under the treatment conditions normally encountered in desalters.

The present invention has demonstrated effective removal of both iron naphthenate species from xylene and is therefore expected to function well with a host of liquid hydrocarbons and iron contaminants.

Although the invention has been generally described for use in conjunction with petroleum crudes, other environments are contemplated. In fact, the present invention is thought to be applicable to the extraction of iron from any iron containing liquid hydrocarbon. For example, in the manufacture of ethylene dichloride (EDC), ethylene is chlorinated with the use of an iron containing catalyst. Carryover of the iron containing catalyst with the desired product during product purification diminishes the value and performance of the ethylene dichloride.

EXAMPLES

In order to demonstrate the efficacy of the inventive method in extracting organic soluble iron species, the following evaluation was performed.

PROCEDURE

Unless otherwise noted, 95 ml (0.095 mmol or 0.000095 mol or 95×10^{-6} or 56 ppm of Fe) of iron naphthenate in xylene (or crude oil), 5 ml of water, and the required amount of candidate extractant were added to each test flask and used for test purposes. The mixture of xylene and treatment was heated to 180° F. and maintained at that temperature for 20 minutes. Then, water was added and the resulting mixture was stirred for 20 more minutes. Stirring was stopped, the layers were allowed to separate, and the water layer was withdrawn from the bottom opening stopcock of each flask. The withdrawn water phase was then analyzed for iron content via a "wet procedure". A 2M HCl solution was

used to perform two additional extractions on the remaining organic phase to remove the remaining iron so that a total iron balance could be calculated.

Percentage of Fe removal was calculated for each of the test runs. This figure represents the percent of iron extracted by one dosage of the candidate extractant. Fe balance is the total combined mols of iron extracted by the extractant and by the two HCl extractions and is always within 95 ± 15 mmols.

In accordance with the "wet procedure" analytical method, an aliquot of the separated water phase from the flask (0.50 ml) was treated with 0.040 ml of 3% hydrogen peroxide, 3.0 ml of a saturated aqueous ammonium thiocyanate solution, and 4.0 ml of concentrated hydrochloric acid. It was then diluted to 100 ml with deionized water. The percent transmittance of this solution at 460 nm in 2.5 cm cells was determined. Micromoles of Fe for each was then calculated in accordance with the equation

$$\mu \text{ mol Fe} = \frac{\text{ml H}_2\text{O in the extraction} \times (A-0.0315) \times 4.71}{\text{ml H}_2\text{O water tested for Fe analysis}}$$

where A is the absorbance, numerical values derived from a standard curve generated by using a commercial iron standard of 1000 ppm diluted to 56 ppm.

The results of iron extractions with various EDTA formulae are shown in Table II.

TABLE II

Iron Extraction from a Xylene Solution of Iron Naphthenate (95 mL of 0.0010M) Using 5.0 mL of Water

EDTA umol	Molar Ratio MOPA: EDTA	Sol- vent	Wt % EDTA in Formula	Temper- ature C	% Fe Extracted
0	0	—	0	75	9
180	8.6	CA	7.7	25	10
180	8.6	CA	7.7	75	56
180	8.6	CA	7.7	75	33
180	8.6	EH	9.0	25	9
180	8.6	EH	9.0	75	12
200	8.6	EH	9.8	25	5
200	4	EH	9.8	75	7
220	4	EG	10.9	25	8
220	4	EG	10.9	75	16
230	4	W	9.8	75	10
200	4	HG, W(a)	9.8	75	14
200	4	HG	9.8	75	14
260(b)	3	CA	10.0	75	19

(a) 94% HG and 6% W (water)

(b) Nitrilotriacetic acid (NTA)

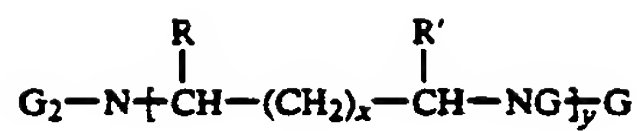
CA = cresylic acid EH = 2-ethylhexanol

EG = ethylene glycol HG = hexylene glycol

The above results show the efficacy of the inventive formulation. What is especially surprising is the ability of the normally hydrocarbon insoluble aminocarboxylic acids, EDTA and NTA, to remove iron from the hydrocarbon medium. This result is achieved by the blending of the specific components of the inventive formulation.

What we claim is:

1. A method of extracting iron species from a liquid hydrocarbon medium comprising adding to the medium a composition comprised of about 2 to 20 weight percent of an amino carboxylic acid having the structure:



where $G = CH_2COOH$, $x = 0$ or 1 , $y = 0$ or 1 and R and R' may be the same or different and are H , CH_3 or $CH_2CH_2CH_2CH_2$, about 3 to 30 weight percent of methoxypropylamine and a solvent selected from the group consisting of 2-ethylhexanol, cresylic acid, ethylene glycol and hexyleneglycol, then adding water to the hydrocarbon medium to form an emulsion, separating the emulsion and removing iron-laden water from the

separated emulsion wherein from about 1-10 moles of the composition is added to the hydrocarbon medium per mole of iron present in the hydrocarbon medium.

2. The method of claim 1 wherein the amino carboxylic acid is selected from the group consisting of ethylenediamine tetraacetic acid, nitrilotriacetic acid, (1,2-propylenedinitrilo)- N,N,N',N' -tetraacetic acid, (1,3-propylenedinitrilo)- N,N,N',N' -tetraacetic acid, (2,3-butylenedinitrilo)- N,N,N',N' -tetraacetic acid and (1,2-diaminocyclohexane)- N,N,N',N' -tetraacetic acid.

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